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# ESTIMATION OF ELECTRON IMPACT EXCITATION CROSS SECTIONS OF MOLECULAR HYDROGEN

*by George M. Prok, Carl F. Monnin, and Henry J. Hettel*

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# ESTIMATION OF ELECTRON IMPACT EXCITATION CROSS SECTIONS OF MOLECULAR HYDROGEN

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Lewis Research Center

## SUMMARY

Cross sections for ionization and excitation of diatomic molecules by electron impact are calculated using a modification of Gryzinski's semiclassical theory. The theoretical model is described. Specific results are given for molecular hydrogen, initially in the ground electronic state, with electron energies ranging up to 360 electron volts. Transitions to principal quantum levels 2, 3, and 4 in both the singlet and triplet systems are considered, including both direct excitation and exchange since there are competing processes. A total cross section for all states above  $n = 4$  is also calculated, as is the ionization cross section. Theoretical direct excitation and exchange cross sections were compared qualitatively with available line intensity data. Good agreement was found both in the shape of the curve and in the location of the peak. The results are compared with experimental ionization data as well as with results based on the Born approximation. In addition, some results for the nitrogen molecule are presented. The results indicate that the molecular model presented in this report gives acceptable estimates of cross sections for excitation of ground-state molecular hydrogen.

## INTRODUCTION

In plasma experiments, a knowledge of the energy loss mechanisms is important. For a tenuous plasma, a major loss mechanism is the radiation produced by inelastic collisions of electrons with molecules or atoms. A knowledge of the cross sections involved is necessary in order to predict the magnitude of this radiation loss. Since a hydrogen plasma contains both atomic and molecular hydrogen species, cross sections for each are required to determine completely the radiation.

Recently, cross sections for atomic hydrogen have become available. Experimental

cross sections have been reported for the  $1s \rightarrow 2s$ ,  $1s \rightarrow 2p$ , and  $1s \rightarrow$  ionization transitions (refs. 1 to 3). Theoretical cross sections for transitions to significant excited states have been calculated by quantum-mechanical techniques and by Gryzinski's semiclassical approach (refs. 3 to 10).

For molecular hydrogen, experimental ionization cross sections are reported in references 11 to 13. Because of the many vibrational and rotational levels involved, the cross sections are difficult to measure. Cross sections for a few electronic transitions have been calculated by the Born approximation (ref. 14, p. 340). From the theoretical standpoint, quantum-mechanical calculations for transitions of interest are tedious. The recent success of Gryzinski's semiclassical approach for calculating the cross sections of atomic transitions makes it attractive for adaptation to molecules. Bauer and Bartky (ref. 15) have reported a way of applying Gryzinski's approach to some diatomic molecules and have obtained satisfactory results. However, their model involves the use of Franck-Condon factors to permit the calculation of cross sections for the excitation of individual vibrational levels. Since the Franck-Condon factors have not been calculated for the 28 excited electronic states of hydrogen, the procedure of Bauer and Bartky could not be directly applied to hydrogen.

If an attempt is made to calculate a total cross section for the excitation of all vibrational levels of a given electronic state, and if the density of vibrational states is high, then the Franck-Condon factors can be ignored without introducing serious errors.

A model based on this assumption is described. The results obtained from this model are compared with available experimental and theoretical molecular hydrogen data. The model was also used to calculate cross sections for molecular nitrogen in order to compare the technique of this report with that of Bauer and Bartky. Transitions were selected for which experimental data are available.

## THEORY AND CALCULATIONS

### Gryzinski's Semiclassical Theory

Considering the inelastic scattering problem as a Coulomb interaction of the incident particle with the bound electron of an atom, Gryzinski developed a classical theory for calculating atomic cross sections (refs. 16 and 17). When the incident particle is an electron, this theory examines both the electron exchange process and the direct excitation process. The cross section for the direct excitation process is given by reference 17 (eqs. (7) and (10)):

$$Q(U_n) = \frac{N_e \sigma_o}{U_n^2} g_j \left( \frac{E_2}{U_n}; \frac{E_1}{U_n} \right) \quad (1)$$

where

$$g_j \left( \frac{E_2}{U_n}; \frac{E_1}{U_n} \right) = \frac{E_1}{E_2} \left( \frac{E_2}{E_1 + E_2} \right)^{3/2} \left\{ \frac{U_n}{E_1} + \frac{2}{3} \left( 1 - \frac{U_n}{2E_2} \right) \ln \left[ 2.72 + \left( \frac{E_2 - U_n}{E_1} \right)^{1/2} \right] \right\} \\ \times \left( 1 - \frac{U_n}{E_2} \right)^{1+E_1/(E_1+U_n)} \quad (2)$$

and

- $E_1$  kinetic energy of bound electron
- $E_2$  kinetic energy of incident electron
- $N_e$  number of equivalent electrons (2 for molecular hydrogen)
- $U_i$  ionization potential
- $U_n$  energy difference between  $n$  level and ground state
- $\sigma_o$   $6.56 \times 10^{-14} \text{ cm}^2 \text{ eV}^2$

The excitation cross section  $Q(U_n)$  is a total cross section for excitation to all levels above  $n$  as well as to  $n$ . To get the direct excitation cross section for the  $n^{\text{th}}$  level, equation (2) must also be applied to the  $n + 1$  level; the difference between the two total cross sections then is the direct excitation cross section for the  $n$  level. Thus, the direct excitation cross sections for the  $n$  level is given by

$$Q(U_n; U_{n+1}) = Q(U_n) - Q(U_{n+1}) \quad (3)$$

For the exchange cross section, Gryzinski assumes that the incident electron replaces one of the bound electrons. The bound electron comes out with an energy less than that of the incident electron depending on the energy level of the final excited state of the atom. The exchange equation is (ref. 17, eqs. (69) and (70))

$$Q_e(U_n) = \frac{N_e \sigma_o}{U_n^2} \frac{U_{n+1} - U_n}{U_n} g_e \left( \frac{U_i}{U_n}; \frac{U_i}{U_{n+1}}; \frac{E_2}{U_n} \right) \quad (4)$$

where

$$g_e \left( \frac{U_i}{U_n}; \frac{U_i}{U_{n+1}}; \frac{E_2}{U_n} \right) = \frac{U_n^2}{(E_2 + U_i)(E_2 + U_i - U_n)} \begin{cases} \frac{U_n}{E_2 + U_i - U_{n+1}} & \text{if } U_{n+1} \leq E_2 \\ \frac{U_n}{U_i} \frac{E_2 - U_n}{U_{n+1} - U_n} & \text{if } U_{n+1} \geq E_2 \end{cases} \quad (5)$$

The  $N_e$  in equation (4) is half that in equation (1), because the probability is 1/2 that the incident electron spin is parallel or antiparallel to the ejected electron. This amounts to assuming that in exchange there is an equal probability of exciting either the singlet or triplet state.

### Molecular Model

Since the Gryzinski theory is one of Coulomb interaction, the variation of electron energy as the molecule vibrates must be known for each electronic state in order to apply this semiclassical theory to a diatomic molecule. The electron energy as a function of internuclear separation for the various electronic states can be described, within the accuracy of Gryzinski's theory, by a Morse curve which is given by (ref. 18, eq. (III 98))

$$V(r - r_e) = D_e \left[ 1 - e^{-\beta(r - r_e)} \right]^2 \quad (6)$$

where

$$\beta = 1.2177 \times 10^7 \omega_e \sqrt{\frac{\mu_A}{D_e}} \quad (7)$$

and

$D_e$	dissociation energy, $\text{cm}^{-1}$
$r$	internuclear separation, cm
$r_e$	internuclear separation in cm at minimum energy for Morse curve
$V(r - r_e)$	energy above minimum energy of Morse curve, $\text{cm}^{-1}$
$\mu_A$	reduced mass in atomic mass units
$\omega_e$	vibrational energy in $\text{cm}^{-1}$ per unit vibrational quantum number

Except for  $D_e$ , the values of the constants for the various excited states of molecular hydrogen are given in reference 18. The dissociation energy  $D_e$  is equal to  $D_0$  plus the zero point energy, where the zero point energy is approximately  $1/2 \omega_e$  (fig. 1). The  $D_0$  values for the various excited states are given in reference 19.

The energy relation between the ground-state potential curve and the potential curve for any excited state of a diatomic molecule such as molecular hydrogen is shown schematically in figure 1. A quantitative relation is given by

$$T(r - r_e)_u = T_{e,u} + V(r - r_e)_u - V(r - r_e)_g \quad (8)$$

where

$T(r - r_e)$	energy difference between ground-state Morse curve and excited-state Morse curve at any given $r$ , $\text{cm}^{-1}$
$T_e$	minimum energy of Morse curve, $\text{cm}^{-1}$
$u$	excited state
$g$	ground state

According to the Franck-Condon principle, electronic excitation takes place at a constant  $r$  because this process is much more rapid than the molecular vibrational motion (ref. 18). This means that, at any given instant of time for an internuclear separation  $r$ , an energy of  $T(r - r_e)_u$  is required to electronically excite state  $u$  for this model. Thus, for the ground electronic and vibrational state of molecular hydrogen, the interaction energy for electronic excitation at the classical turning points  $r_-$  and  $r_+$  is  $T_{r_-}$  and  $T_{r_+}$ , respectively, as shown in figure 1. In terms of Gryzinski's classical theory,

$$T(r - r_e)_u = U_n \quad (9)$$

with  $U_n$  denoted by Gryzinski to be the kinetic energy change of the excited electron. The  $U_n$  is taken to be given by equation (9), but this is strictly true only if the correlation energy of the upper state is equal to the correlation energy of the lower state. When there is a difference between these two, an error is introduced into equation (9) which introduces a smaller error into the calculation of  $Q(U_n)$  by equation (1). However, since  $Q(U_n; U_{n+1})$  is the difference between two values of the total direct excitation cross section, and since the errors are in the same direction, the error introduced in the calculation of  $Q(U_n; U_{n+1})$  is significantly smaller than the error introduced in the values of  $U_n$  and  $U_{n+1}$  when ignoring the effect of electron correlation energy in the bond.

From figure 1 it can be seen that for any given electronic excitation the value of  $U_n$  will vary with the internuclear separation. Since Gryzinski's equations can only be applied to a system of energy levels whose energy separations are constant, Gryzinski cross sections can be calculated for only one value of  $r$  at a time. The cross sections, therefore, as a function of  $r$  can be appropriately averaged to give an overall cross section for a molecular system.

The probability that the internuclear separation is a given value of  $r$  can be approximated by the probability density distribution of a harmonic oscillator, which is given by (ref. 18, eq. (III 38))

$$|\psi_v|^2 = |N_v e^{-1/2(\alpha x^2)} H_v(\sqrt{\alpha} x)|^2 \quad (10)$$

where

$H_v(\sqrt{\alpha} x)$	Hermite polynomial of $v^{\text{th}}$ degree
$N_v$	normalization factor
$x$	displacement of oscillator from average value, $(r - r_e)$
$\alpha$	$6.518 \times 10^{17} \text{ cm}^{-2}$ for molecular hydrogen
$\psi_v$	vibrational eigenfunction

The normalization factor for any vibrational level  $v$  is given by

$$N_v = \sqrt{\frac{1}{2^v v!}} \sqrt{\frac{\alpha}{\pi}} \quad (11)$$

For the lowest vibrational level  $v = 0$ , the probability distribution is

$$\psi_0^2 = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha x^2} \quad (12)$$



For any given vibrational level, a weighting factor  $F$  to be applied to the Gryzinski cross section obtained at a constant  $r$  can be determined from equation (10). The Gryzinski cross section  $Q$  (direct excitation or exchange cross section) for a given transition then becomes

$$Q = \sum_{j=1}^{j=i} F_j Q_j \quad (13)$$

where

$$\sum_{j=1}^{j=i} F_j = 1 \quad (14)$$

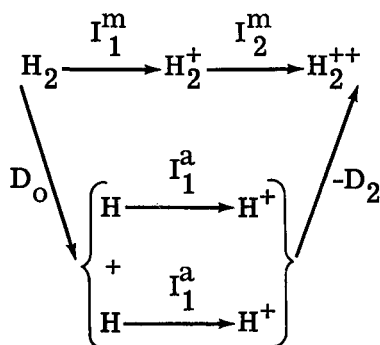
where  $i$  is the number of increments into which the probability density distribution curve was divided, and  $F_j$  is the average value of equation (10) subtended by the  $j^{\text{th}}$  piece. At low internuclear separations there is some crossing of the various molecular hydrogen Morse curves. Thus, when calculating the cross section for a given level  $n$ , the level of next higher energy, that is,  $n + 1$ , may not be always the same one for all  $r$  values. At the level crossing point, a different molecular state may become the  $n + 1$  level, and care must be taken to use this different state as the  $n + 1$  level.

In obtaining the cross section for molecular hydrogen, both the direct excitation and exchange processes were assumed applicable to the singlet system. For the triplet system, only the exchange process is applicable. In calculating the singlet system cross sections, the presence of triplet states was ignored. Hence, when a given singlet level was designated  $n$ , the level  $n + 1$  was taken to be the next highest energy singlet level even when a triplet level intervened. Similarly, the presence of singlet levels was ignored when calculating the cross sections of the triplet system states.

The dissociative transition  $X^1\Sigma_g^+ \rightarrow 2^3\Sigma_u^+$  was not computed because cross sections for this transition are available (ref. 20) and there is no molecular radiation loss from the  $2^3\Sigma_u^+$  state. Only the results of excitation from the ground vibrational state of molecular hydrogen to upper states that radiate are presented. These excited states are shown in table I. The threshold energies are shown on an energy level diagram in figure 2.

In order to apply Gryzinski's method, the kinetic energy of the bound electrons must be determined. The quantity  $E_1$  is taken by Gryzinski (ref. 16) to be the first molecular ionization potential. This is inconsistent with his apparent usage of  $E_1$  to be the average energy of the equivalent electrons, in the same paper, for the case of helium.

The quantity  $E_1$  is calculated in this latter connotation by means of the following chemical equations involving equivalent processes:



wherein  $I_1^m$  and  $I_2^m$  are the first and second molecular ionization potentials,  $I_1^a$  the atomic ionization potential,  $D_0$  the dissociation energy of the neutral molecule, and  $D_2$  the dissociation energy of the doubly ionized molecule. Thus, if  $E_1$  is the average energy of the two electrons in the ground state of molecular hydrogen,

$$E_1 = \frac{1}{2} (I_1^m + I_2^m) = \frac{1}{2} (D_0 + 2I_1^a - D_2) \quad (15)$$

To calculate  $E_1$  requires only that  $D_2$  be evaluated, but this is straightforward since it is unequivocally the coulombic energy of two protons separated to the internuclear distance of molecular hydrogen. Thus,

$$D_2(H_2^{++}) = \frac{e^2}{r} = -19.40 \text{ eV} \quad (16)$$

Insertion of this value into equation (16), together with  $D_0 = 4.48$  electron volts and  $I_1^a = 13.60$  electron volts, yields an  $E_1$  of 25.54 electron volts for ground state molecular hydrogen.

Because of the number of computing steps involved and the large number of states molecular hydrogen has, it was impractical to hand calculate the desired cross sections. All cross section results, therefore, were obtained by means of an electronic computer.

## RESULTS AND DISCUSSION

### Molecular Hydrogen

The cross section for directly exciting levels with principal quantum numbers of 2, 3, and 4 are shown in figures 3 to 5, respectively. Figure 5(d) shows the total direct excitation cross section of the  $S^1\Delta_g$  and all higher levels to, but not including, ionization. The calculated cross section for the level that Herzberg calls Q (ref. 18) is shown in figure 6. This Q level was included in the calculation because spectral data indicates it is a singly excited state (ref. 18). If Q is, however, a doubly excited state, its cross section should not be included in this report, and the cross sections reported herein from the ground state to  $E^1\Sigma_g^+$ ,  $C^1\Pi_u$ ,  $G^1\Sigma_g^+$ , and  $D^1\Pi_u$  should be increased by 40, 18, 17, and 16 percent, respectively.

The singlet exchange cross sections are shown in figures 7 to 10 for principal quantum levels 2, 3, and 4, and for level Q, respectively. The triplet exchange cross section for principal quantum levels 2, 3, and 4 are shown in figures 11 to 13, respectively. A total exchange cross section for all the remaining triplet levels is shown in figure 14.

Born approximation results for  $X^1\Sigma_g^+ \rightarrow E^1\Sigma_g^+$ ,  $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ ,  $X^1\Sigma_g^+ \rightarrow C^1\Pi_u$ , and  $X^1\Sigma_g^+ \rightarrow D^1\Pi_u$  transitions are reported in reference 14 for 100-, 200-, and 300-electron-volt incident electrons. These are compared in figures 3 and 4(b) with the results of the present work. The results presented compare very well with the Born approximation for  $n = 2$ ; however, for the single comparison at  $n = 3$ , the Born approximation gives values more than three and a half times greater than the  $X^1\Sigma_g^+ \rightarrow D^1\Pi_u$  values reported herein.

Experiment, however, is the only true test for cross section approximations. The only experimental results available for comparison are relative line intensity results reported in references 21 and 22. Figure 15 compares the calculated singlet direct excitation and exchange curve shapes for the  $X^1\Sigma_g^+ \rightarrow G^1\Sigma_g^+$  with Kruithof and Ornstein's experimental relative line intensity resulting from this transition. For ease of comparison of the curve shapes, the line intensity maximum was normalized separately to both the direct excitation and exchange maxima. It is evident from figure 15 that both direct excitation and exchange are probably taking place for this transition. For the curve shape, however, better agreement with experiment is obtained by using the direct excitation rather than the exchange process. Figure 16 compares the computed triplet exchange with experimental relative line intensity, resulting from an  $X^1\Sigma_g^+ \rightarrow k^3\Pi_u$  transition, where the experiment was again normalized at the maximum of the computed results. As can be seen from the figure, the experimentally determined variation of cross section closely resembles the calculated one.

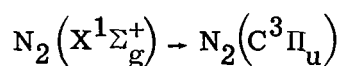
The location of the peak is very nearly the same for both curves; the experimental results indicate a less rapid decline in cross section at the higher energies.

The computed ionization results are shown in figure 17 for both  $E_1 = 15.4$  and 25.5 electron volts. Comparing these results with experimental results reported in reference 13 shows good agreement. The present results for  $E_1 = 15.4$  electron volts are in good agreement with results for the ionization cross section reported in Gryzinski's first paper (ref. 16) for the same  $E_1$ . This appears to be entirely coincidental, however, because in his first paper Gryzinski's equations assumed a constant kinetic energy for the bound electrons. A later paper by Gryzinski (ref. 17) eliminated the constraint of constant kinetic energy for the bound electrons from the equations. The equations from this later publication were the ones used in the present work. Although either choice for the value of  $E_1$  produces a relation closely matching that obtained experimentally, the higher value ( $E_1 = 25.5$  eV) seems to give the best results. The slope of this curve at the high electron energies is almost identical with that of the experimental curve.

The cross sections calculated using the Gryzinski approach and reported herein generally agree with experimental results and with Born approximations where such comparisons are possible. They should, therefore, be adequate for applications such as estimating energy balances within tenuous plasmas.

## Molecular Nitrogen

A comparison of the molecular model presented here with the work of Bauer and Bartky (ref. 15) was made for molecular nitrogen. For the exchange process



and when the same  $N_e$ ,  $U_n$ ,  $U_{n+1}$  and  $U_i$  are used as in reference 15, the results of the present model agree with those of Bauer and Bartky to within a few percent. Similarly, the total cross section for the ionization of nitrogen calculated from the model used herein agrees closely with that calculated by Bauer and Bartky if the same data are used in the model of this report that Bauer and Bartky used in theirs. However, it is questionable whether the values of  $E_1$  used in the ionization calculations are correct. The ionization process treated herein is now examined in greater detail.

The total ionization cross section presented in figure 18 is the sum of the cross sections for the three following individual processes:

Process		Ionization potential
$N_2(X^1\Sigma_g^+)$	$\xrightarrow{-e(2p\sigma_g)} N_2^+(X^2\Sigma_g^+)$	15.6
$N_2(X^1\Sigma_g^+)$	$\xrightarrow{-e(2p\pi_u)} N_2^+(A^2\Pi_u)$	16.7
$N_2(X^1\Sigma_g^+)$	$\xrightarrow{-e(2s\sigma_u)} N_2^+(B^2\Sigma_u^+)$	18.8

Bauer and Bartky took  $E_1$  to be equal to the ionization potential for each process, yielding the result designated "reference 15, Bauer and Bartky" in figure 18. Using the ionization potentials for  $E_1$  in the model of this report yielded the curve designated "present work,  $E_1$  = ionization potential."

If, however, the average energies of the equivalent electrons in each orbital type are calculated with the aid of references 18, 23, and 24, as shown in appendix B, one finds that  $E_1(2p\sigma_g) = 21.8$  electron volts,  $E_1(2p\pi_u) = 37.7$  electron volts, and that  $E_1(2s\sigma_u) = 24.1$  electron volts (table II). These values of  $E_1$  when inserted into the model of this report, yield the curve in figure 18 entitled "present work,  $E_1$  = average orbital electron energy." This curve appears to resemble most closely the shape of the experimental curves, although it predicts high values of the cross section.

## CONCLUDING REMARKS

A molecular model was developed for adapting Gryzinski's equations to estimate both direct excitation and exchange cross sections of molecular hydrogen. From a comparison of the calculated cross sections with relative line intensity experimental results, singlet transitions which are optically unallowed seem to go to excited states by both the exchange and direct excitation processes. Applying the present method to molecular nitrogen indicates that it might be possible to use the same procedure on other diatomic molecules. In any case, the cross sections presented in this report are the only ones available for many of the molecular hydrogen transitions. Until more extensive experimental data become available, these cross sections can be used to estimate the energy loss by line radiation and the energy requirements for ion production in tenuous hydrogen plasmas.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, February 10, 1967,  
129-01-05-09-22.

# APPENDIX A

## SYMBOLS

$D_e$	dissociation energy, $\text{cm}^{-1}$	$Q(U_n; U_{n+1})$	direct excitation cross section defined by eq. (3), $\text{cm}^2$
$D_0$	dissociation energy less the zero point energy, $\text{cm}^{-1}$	$r$	internuclear separation, cm
$E_1$	kinetic energy of bound electron (for molecular hydrogen $E_1 \cong U_i$ ), eV	$r_e$	internuclear separation at minimum energy of Morse curve, cm
$E_2$	kinetic energy of incident electron, eV	$T_e$	minimum energy of Morse curve, $\text{cm}^{-1}$
$e$	electronic charge, esu	$T(r - r_e)$	energy difference between ground-state and excited-state Morse curves at constant $r$ , $\text{cm}^{-1}$
$F$	weighting factor for cross sections at a given $r$	$U_i$	ionization potential in Gryzinski equations, $\text{cm}^{-1}$
$g_e$	defined by eq. (5)	$U_n$	energy of level $n$ above ground state, $\text{cm}^{-1}$
$g_j$	defined by eq. (2)	$V(r - r_e)$	energy above minimum energy of Morse curve, $\text{cm}^{-1}$
$H_v(\sqrt{\alpha}x)$	Hermite polynomial of $v^{\text{th}}$ degree	$v$	vibrational level
$I$	ionization potential in thermodynamic cycle, eV	$x$	displacement of harmonic oscillator from average value, $(r - r_e)$
$i$	number of increments into which probability density distribution was divided	$\alpha$	$6.518 \times 10^{17} \text{ cm}^{-2}$ , for molecular hydrogen
$N_e$	number of equivalent electrons	$\beta$	defined by eq. (7)
$N_v$	normalization factor	$\mu_A$	reduced mass (in atomic mass units)
$n$	energy level	$\sigma_0$	$6.56 \times 10^{-14} \text{ cm}^2 \text{ eV}^2$
$Q$	any cross section, $\text{cm}^2$		
$Q_e(U_n)$	exchange cross section, $\text{cm}^2$		
$Q(U_n)$	total direct excitation cross section (excitation cross section from Gryzinski's theory), $\text{cm}^2$		

$\psi_v$  vibrational eigenfunction  
 $\omega_e$  vibrational energy per unit vibrational quantum number,  $\text{cm}^{-1}$

Subscripts:

1 first ionization potential  
2 second ionization potential  
g ground electronic state

n energy level  
u excited electronic state  
v vibrational level

Superscripts:

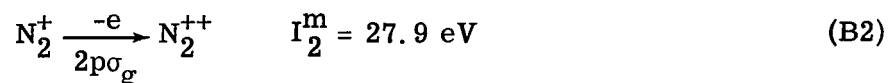
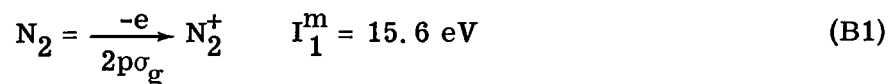
a atomic  
m molecular

## APPENDIX B

### CALCULATION OF AVERAGE ENERGIES OF EQUIVALENT ORBITAL ELECTRONS

The procedure used by Gryzinski to obtain the average energy  $E_1$  of the electrons in any atomic subshell is to calculate the linear average of the sequential ionization potentials of these electrons. This procedure may be, in principle at least, directly applied to molecules.

Consider the case of the two  $2p\sigma_g$  electrons in molecular nitrogen. The reactions involved are



Thus,  $E_1(2p\sigma_g)$ , the average energy of the two electrons in the  $2p\sigma_g$  orbital is given by

$$E_1(2p\sigma_g) = \frac{I_1^m + I_2^m}{2} \quad (B3)$$

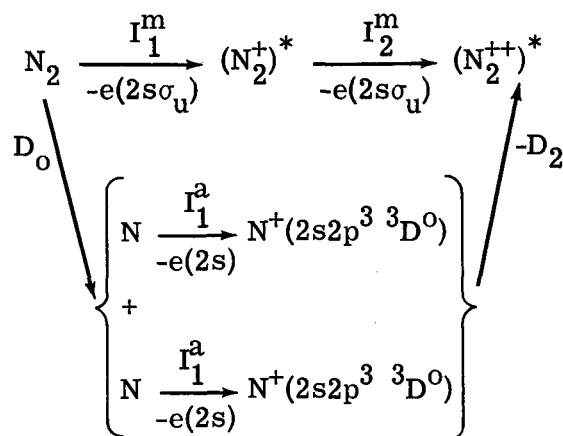
which yields 21.8 electron volts for the average energy of each  $2p\sigma_g$  electron.

The case considered now is of the two  $2s\sigma_u$  electrons. The question to be answered is how much energy is required to remove these two electrons from the molecule. The reactions involved are



but the molecular ionization potentials for these reactions are not known. It is possible, however, to calculate the energy involved by means of the following equivalent processes:



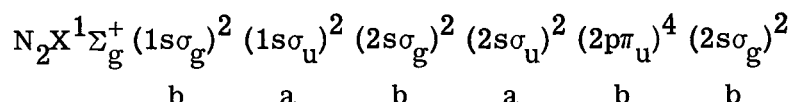


Thus,

$$I_1^m + I_2^m = D_0 + 2I_1^a - D_2 \quad (\text{B6})$$

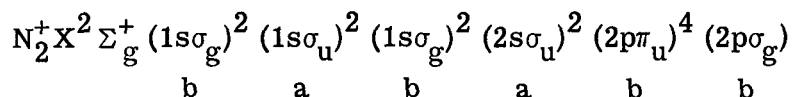
wherein  $D_0$  is the energy for dissociation into ground-state atoms, of value 9.76 electron volts, and  $I_1^a$  is the energy for the production of the excited atomic ion which results upon removal of a 2s electron from the atom, the value of which is 25.98 electron volts. Unfortunately,  $D_2$  for the excited molecular ion  $(\text{N}_2^{++})^*$  is not known; therefore, only an educated guess can be made of its magnitude.

The electron configuration of the ground state of molecular nitrogen is



wherein b designates a bonding orbital and a designates an antibonding orbital. If one ignores the tendency of an antibonding orbital to be more antibonding than a bonding orbital is bonding, it can be assumed that corresponding bonding and antibonding orbital energies cancel one another. It may then be further assumed that the 9.76 electron-volt dissociation energy of the  $\text{X}^1\Sigma_g^+$  state is equally divided among the six remaining bonding electrons, so that each electron contributes 1.63 electron volts to the total.

Next is considered the ground state of  $\text{N}_2^+$ , whose electron configuration is



The dissociation energy of this state, 8.72 electron volts, divided among the five bonding electrons yields an average bonding energy for each electron of 1.74 electron volts.



at the internuclear separation of  $N_2$ . Thus,  $D_4$  is approximated to be - 52.6 electron volts. Insertion of this value into equation (B8), together with  $D_0 = 9.76$  electron volts,  $I_1^a = 14.54$  electron volts, and  $I_2^a = 29.61$  electron volts, yields a value for  $E_1(2p\pi_u)$  of 37.7 electron volts.

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TABLE I. - ELECTRONIC STATES OF MOLECULAR  
HYDROGEN USED IN CROSS-SECTION  
CALCULATIONS

Singlet system			Triplet system		
Principal quantum number	Herzberg's designation	Term symbol	Principal quantum number	Herzberg's designation	Term symbol
2	E	$1\Sigma_g^+$	2	a	$3\Sigma_g^+$
2	B	$1\Sigma_u^+$	2	c	$3\Pi_u$
2	C	$1\Pi_u$	3	h	$3\Sigma_g^+$
3	H	$1\Sigma_g^+$	3	e	$3\Sigma_u^+$
3	D	$1\Pi_u$	3	d	$3\Pi_u$
3	G	$1\Sigma_g^+$	3	i	$3\Pi_g$
3	I	$1\Pi_g$	3	j	$3\Delta_g$
3	J	$1\Delta_g$	4	f	$3\Sigma_u^+$
4	$^aO$	$1\Sigma_g^+$	4	k	$3\Pi_u$
4	$^aP$	$1\Sigma_g^+$	4	p	$3\Sigma_g^+$
4	R	$1\Pi_g$	4	r	$3\Pi_g$
4	$^aS$	$1\Delta_g$	4	s	$3\Delta_g$
-----	$^bQ$	$1\Pi_g$	4	m	$3\Sigma_u^+$
Ionization	---	----	4	$^c_v$	$3\Pi_g$

$^a\omega_e$  estimated to be 2200.

$^bD_0$  estimated to be 2.60.

$^cD_0$  estimated to be 2.70.

TABLE II. -  $N_2^+$  DATA FOR CALCULATING  
CROSS SECTION FOR  $N_2^+$  FROM  $N_2$

State of $N_2^+$ molecule	Electron configuration of subshell	Ionization potential, eV	Average kinetic energy of electron, eV
$X^2\Sigma_g^+$	$(\sigma_g)^2$	15.6	21.8
$A^2\Pi_u$	$(\pi_u)^4$	16.7	37.7
$B^2\Sigma_u^+$	$(\sigma_u)^2$	18.8	24.1

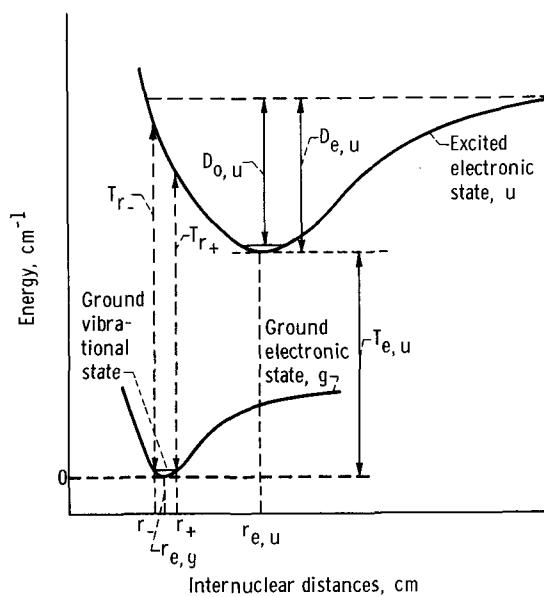


Figure 1. - Model for calculating energies involved in exciting diatomic molecules.

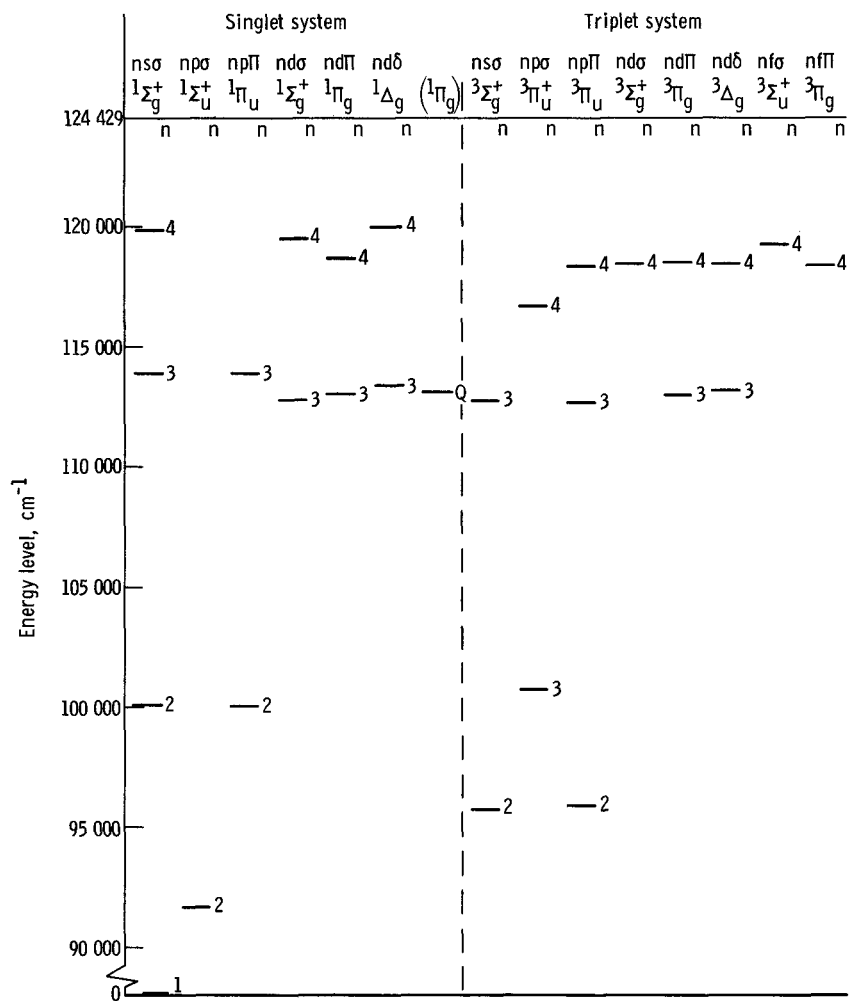
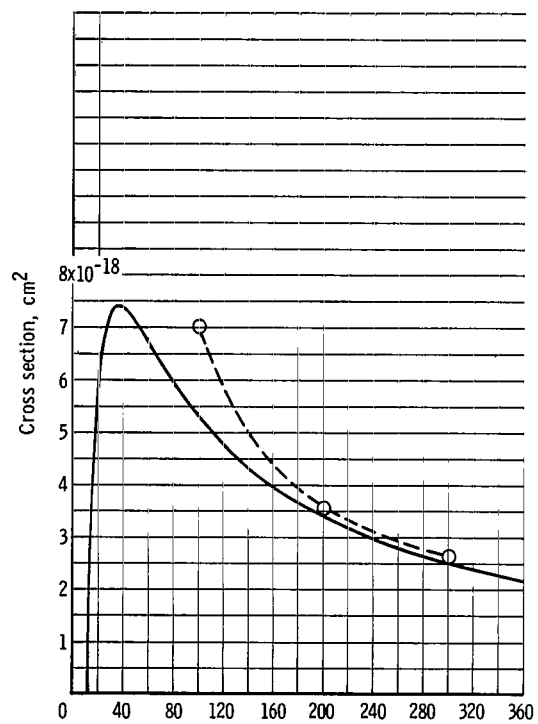
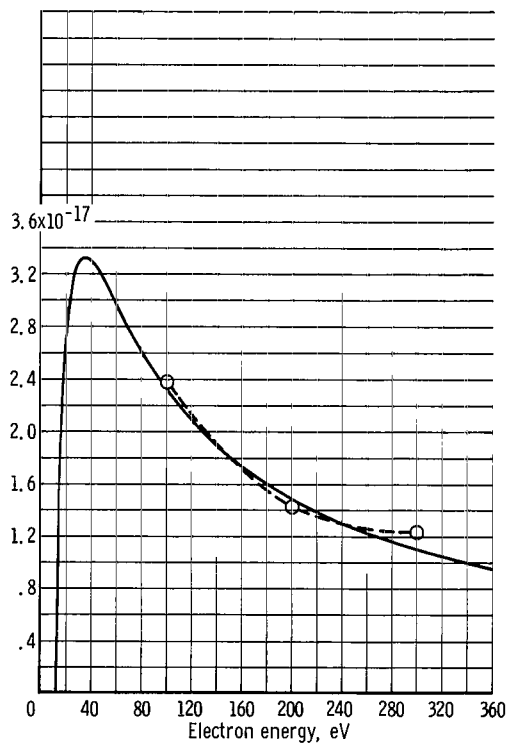


Figure 2. - Energy level diagram (ref. 18) for electronic states of molecular hydrogen considered in present report. (Since the electronic configuration of Q is not known, Herzberg's designation was used.)

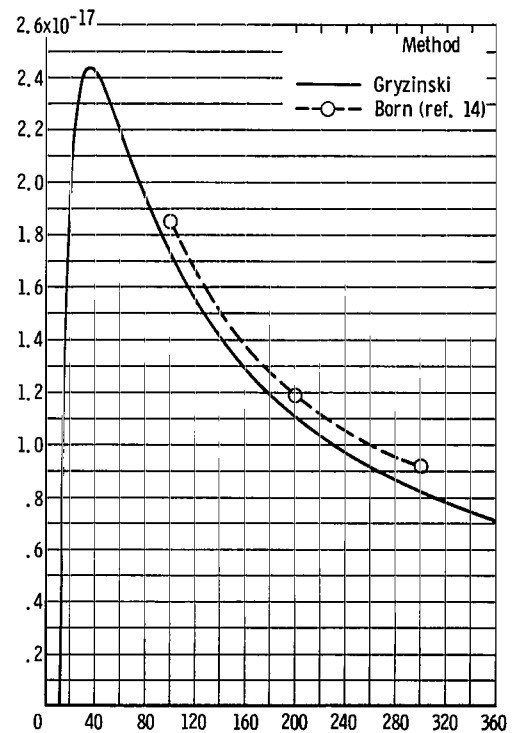




(a) Cross section for  $X^1\Sigma_g^+ \rightarrow E^1\Sigma_g^+$ .



(b) Cross section for  $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ .



(c) Cross section for  $X^1\Sigma_g^+ \rightarrow C^1\Pi_u$ .

Figure 3. - Direct excitation cross sections to principal quantum level 2 of molecular hydrogen.

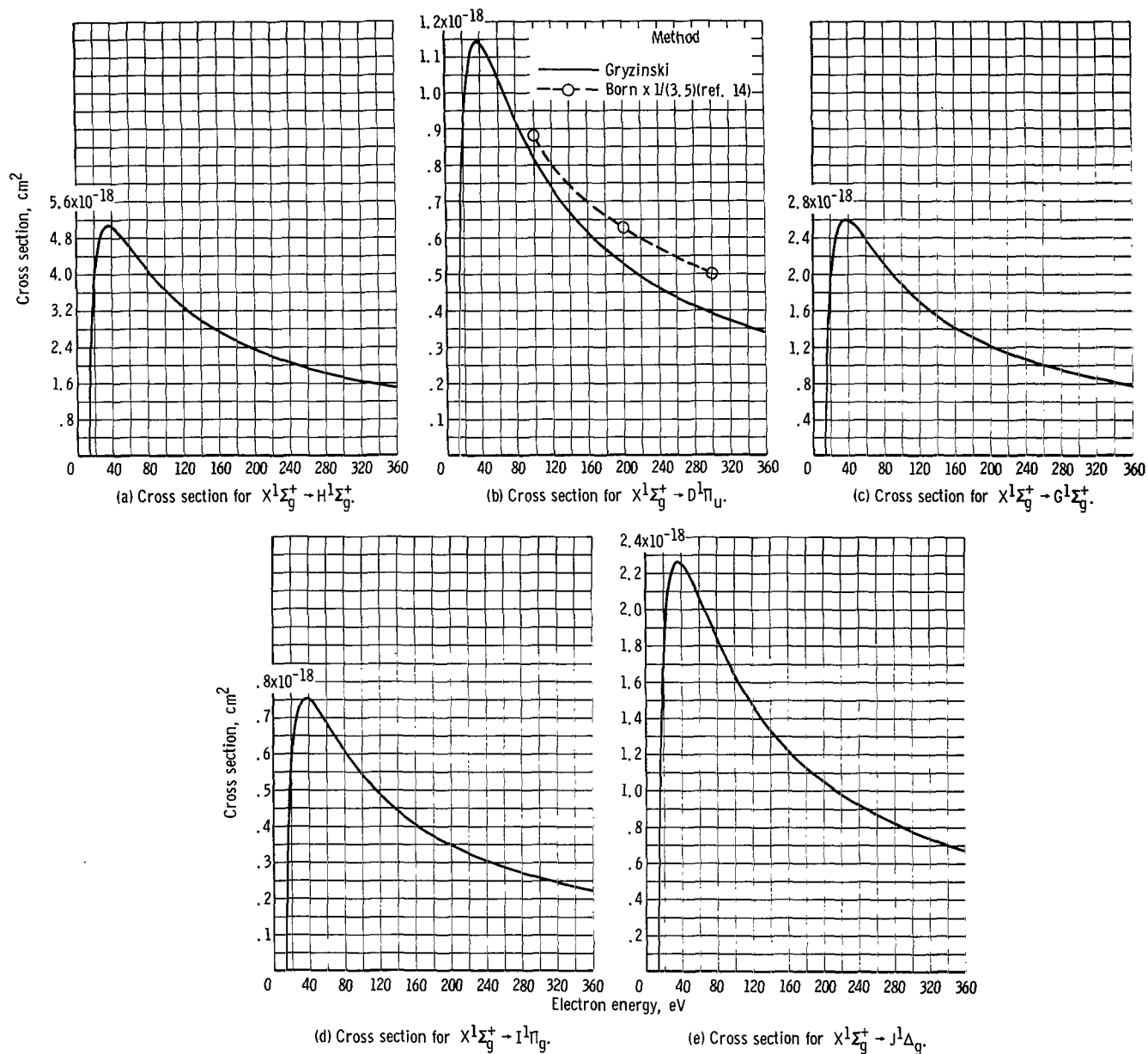


Figure 4. - Direct excitation cross section to principal quantum level 3 of molecular hydrogen.

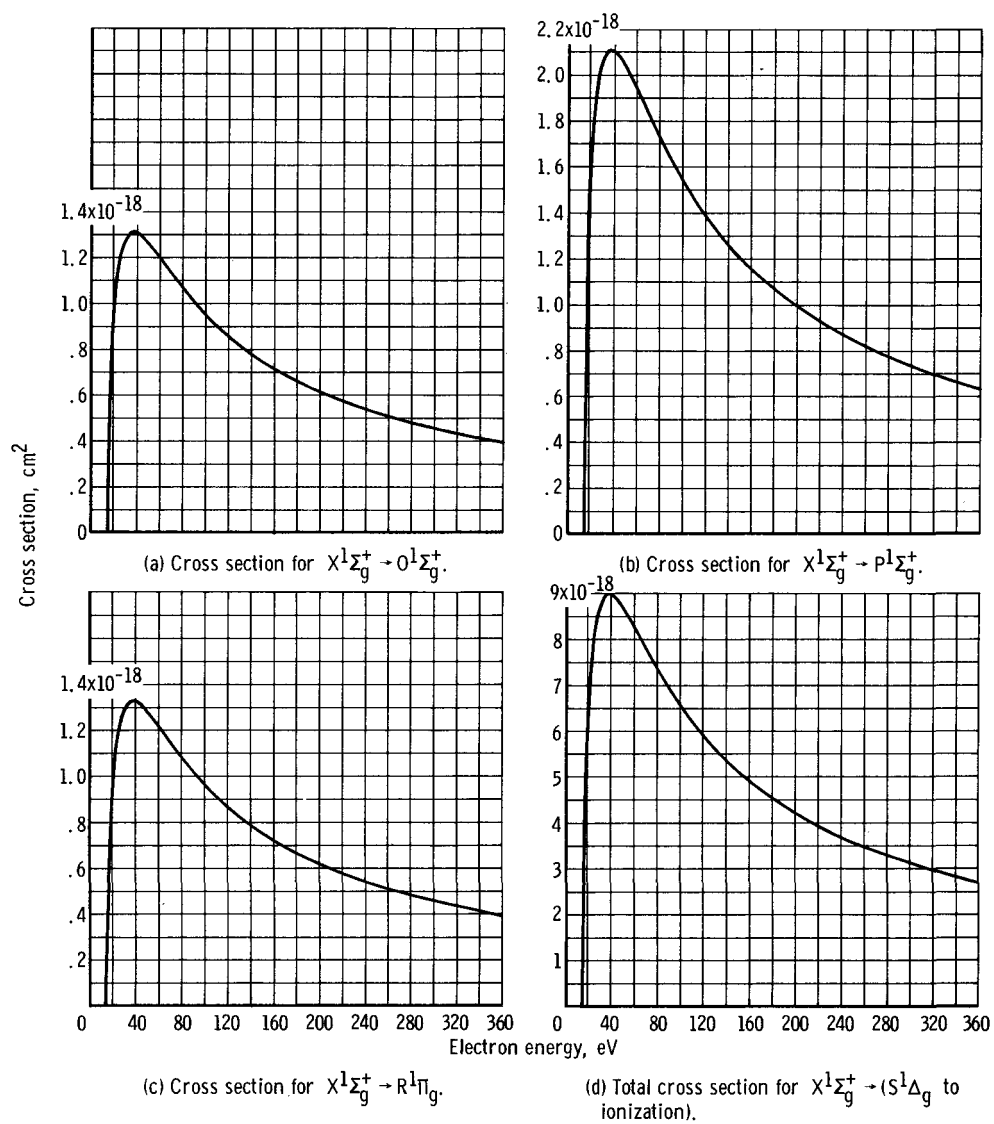


Figure 5. - Direct excitation cross sections to principal quantum level 4 of molecular hydrogen.

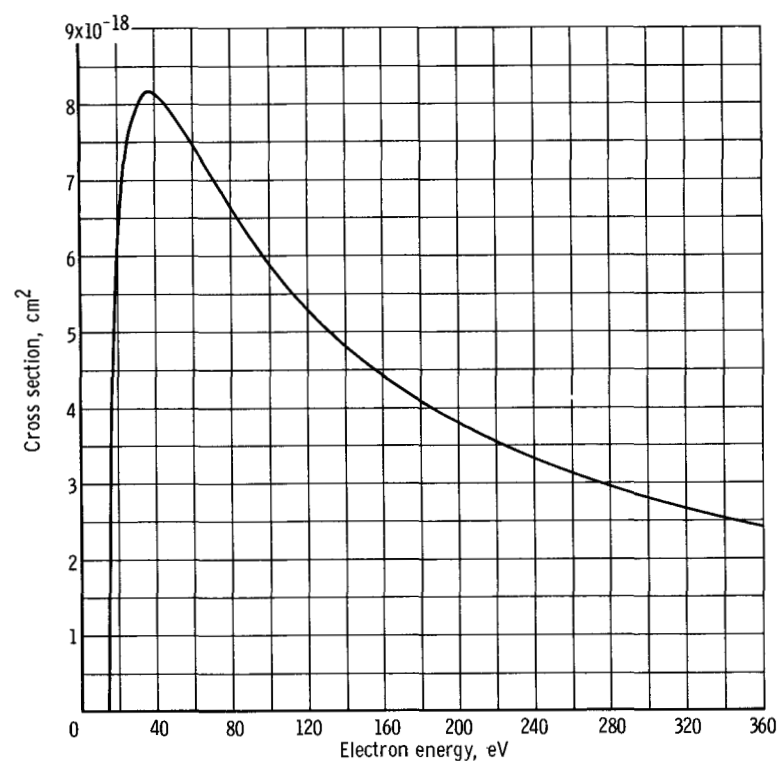
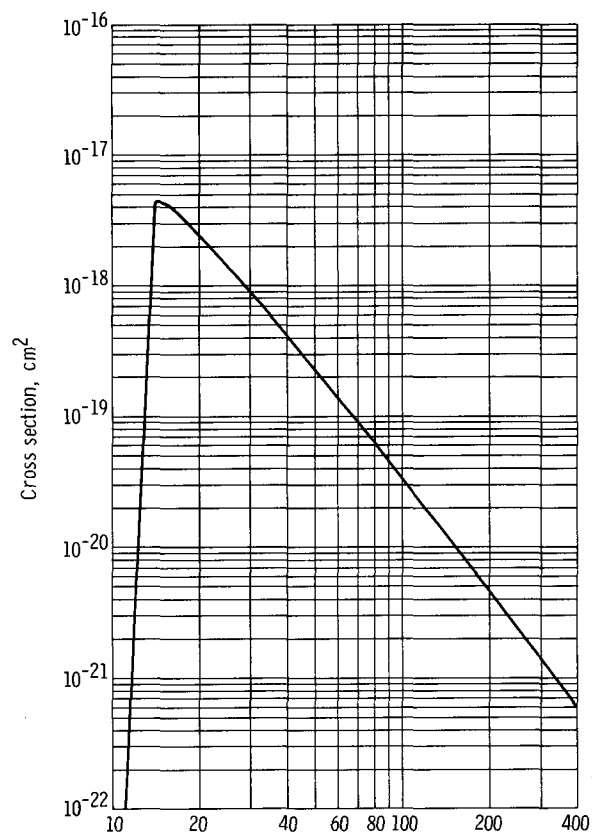
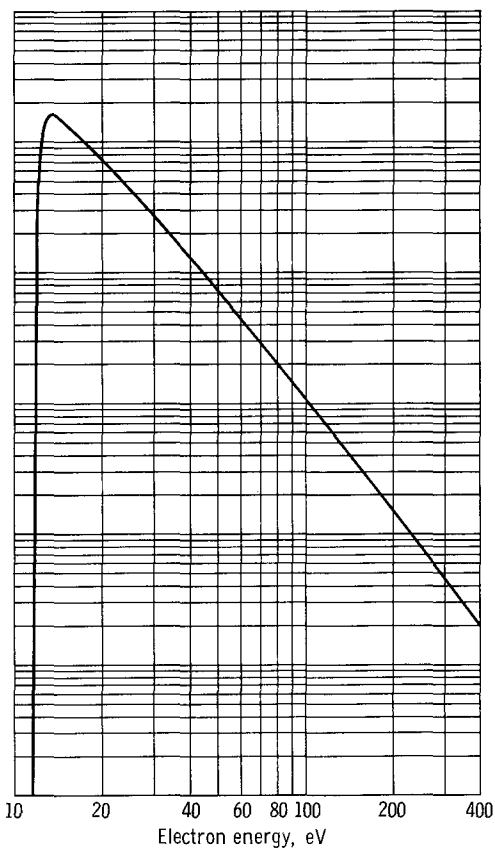


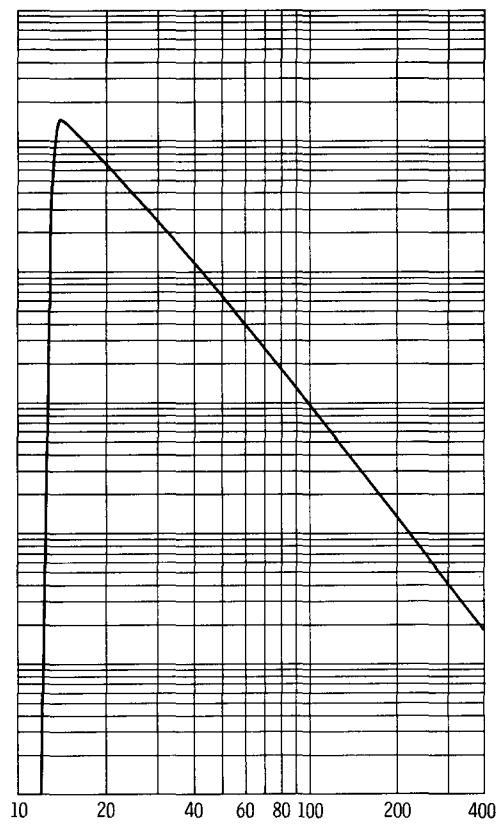
Figure 6. - Direct excitation cross section to level Q of molecular hydrogen (assumed to be singly excited). Cross section for  $X^1\Sigma_g^+ \rightarrow Q^1\Pi_g$ .



(a) Exchange cross section for  $X^1\Sigma_g^+ \rightarrow E^1\Sigma_g^+$ .



(b) Exchange cross section for  $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ .



(c) Exchange cross section for  $X^1\Sigma_g^+ \rightarrow C^1\Pi_u$ .

Figure 7. - Singlet exchange cross sections to principal quantum level 2 of molecular hydrogen.

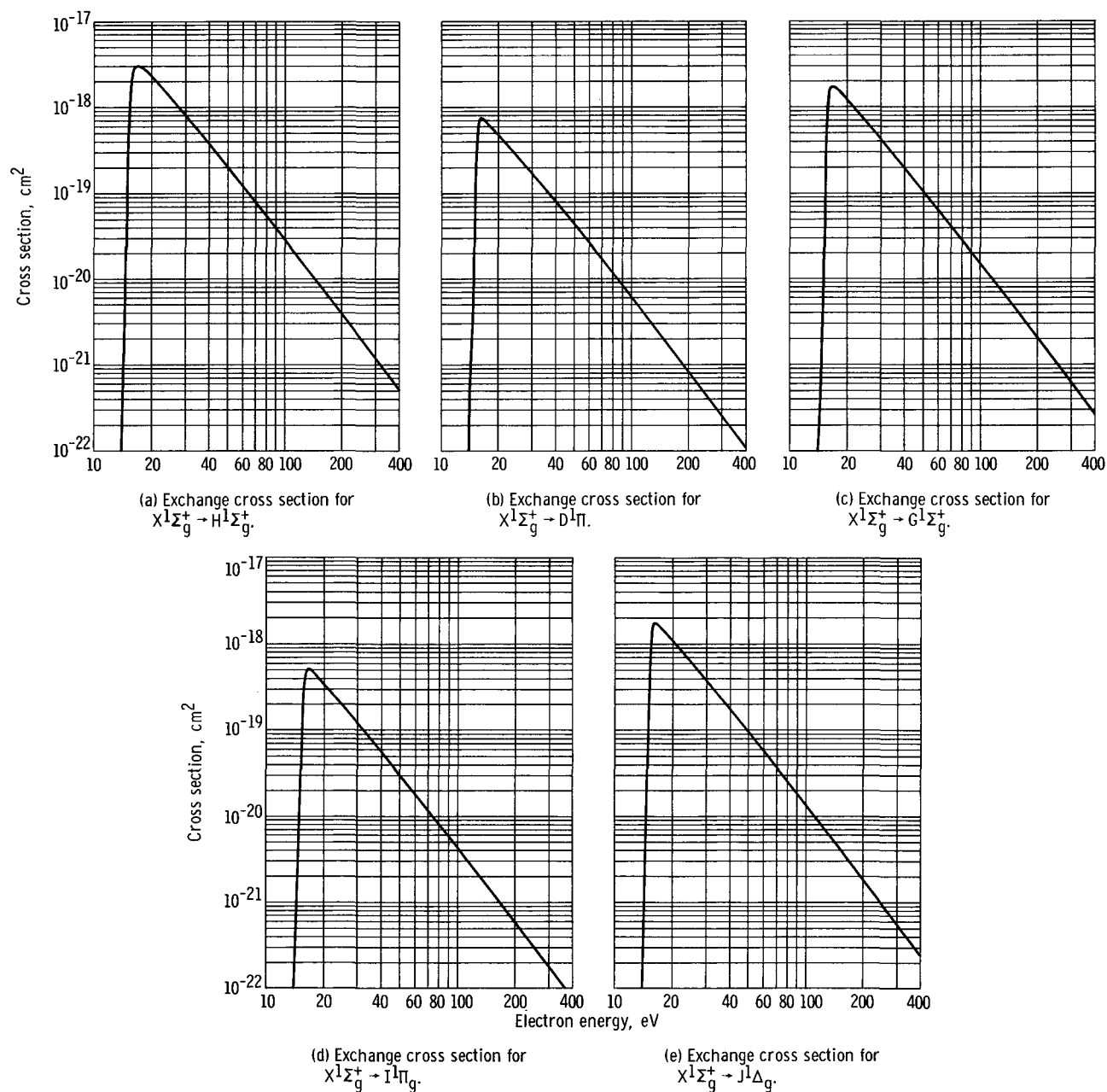


Figure 8. - Singlet exchange cross sections to principal quantum level 3 of molecular hydrogen.

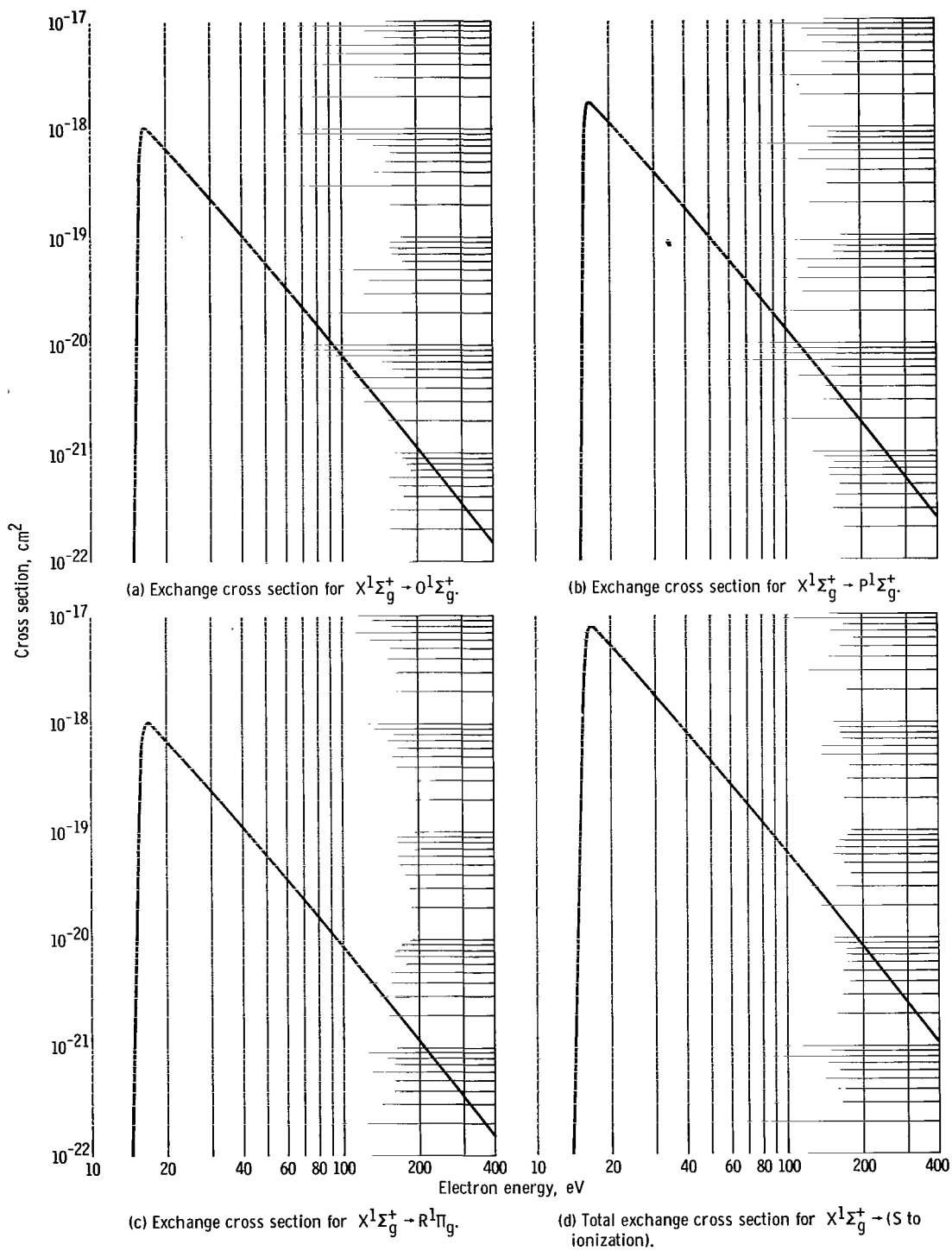


Figure 9. - Singlet exchange cross sections to principal quantum level 4 of molecular hydrogen.

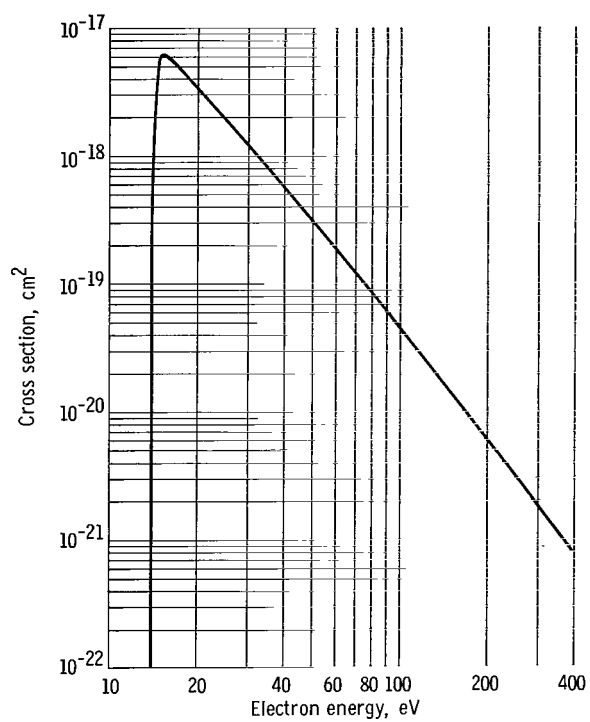
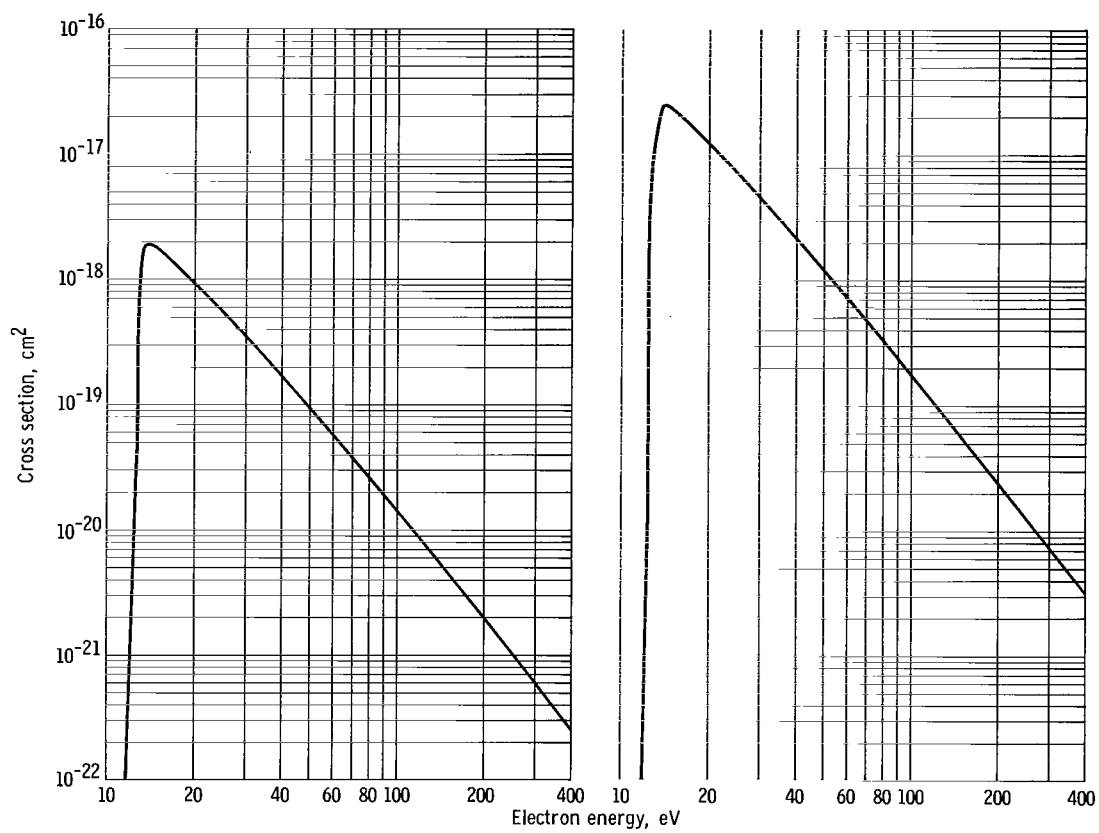


Figure 10. - Singlet exchange cross section to level Q of molecular hydrogen. Exchange cross section for  $X^1\Sigma_g^+ \rightarrow Q^1\Pi_g$ .





(a) Exchange cross section for  $X^1\Sigma_g^+ \rightarrow a^3\Sigma_g^+$ .

(b) Exchange cross section for  $X^1\Sigma_g^+ \rightarrow c^3\Pi_u$ .

Figure 11. - Triplet exchange cross sections to principal quantum level 2 of molecular hydrogen.

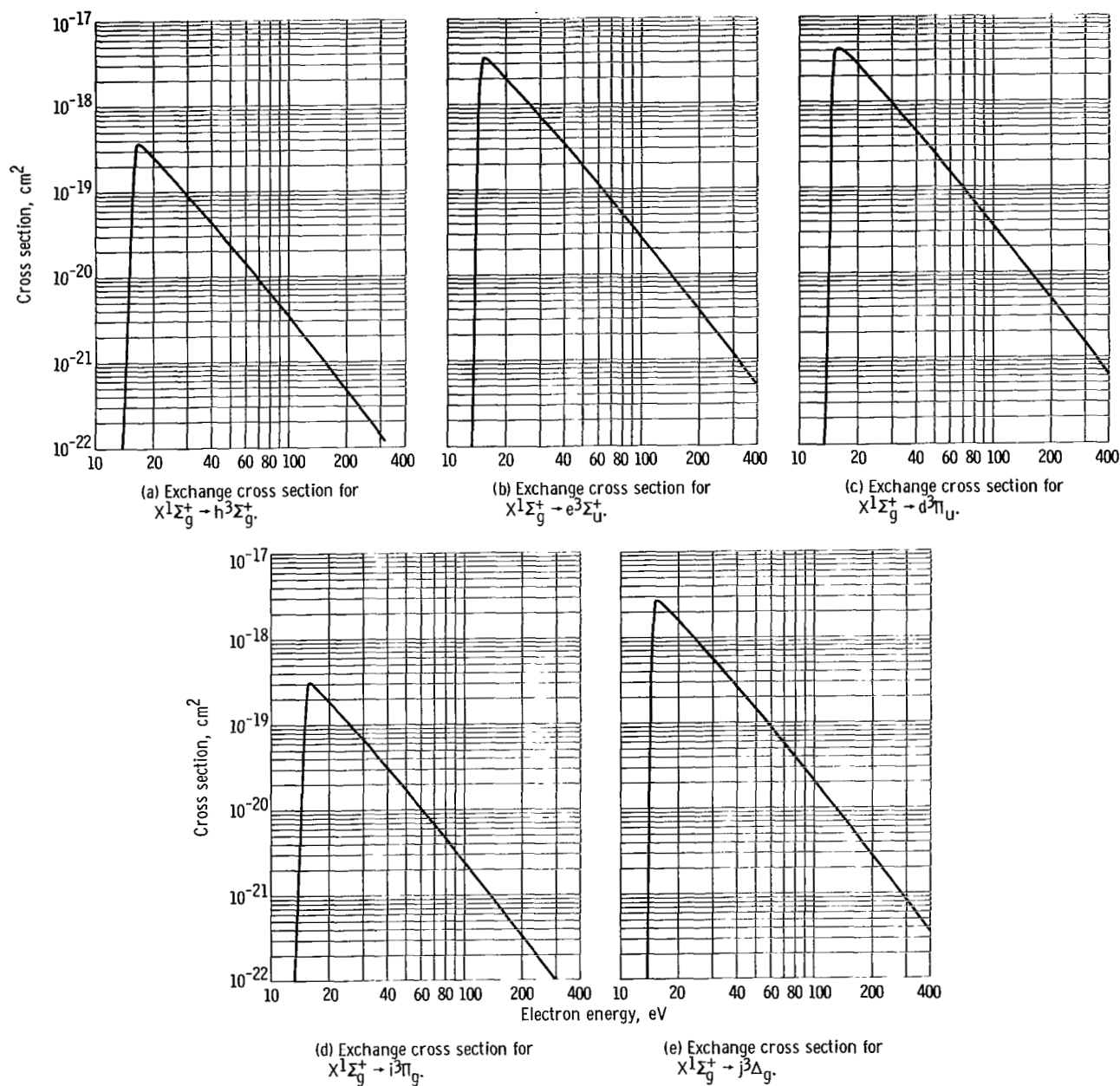


Figure 12. - Triplet exchange cross sections to principal quantum level 3 of molecular hydrogen.

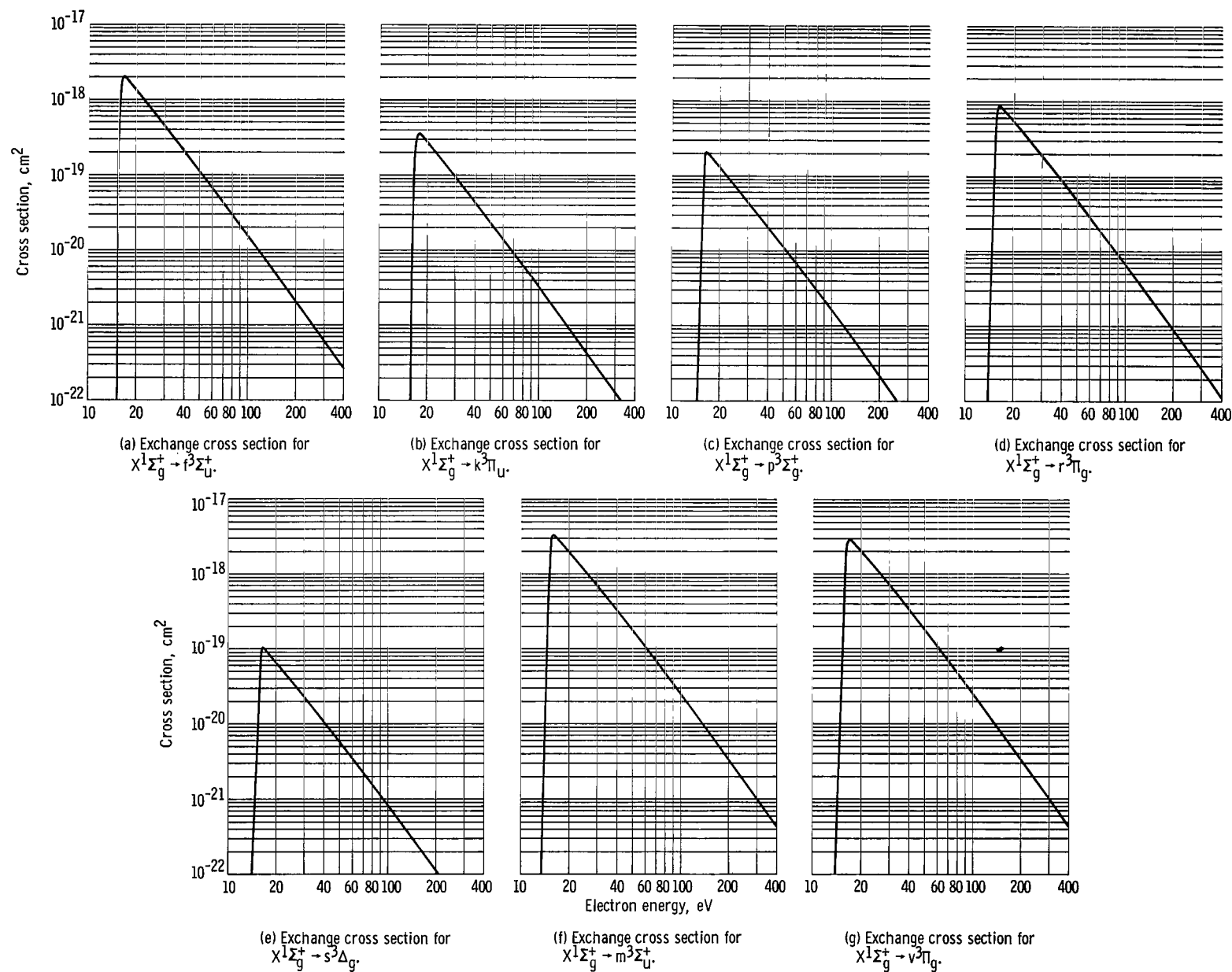


Figure 13. - Triplet exchange cross sections to principal quantum level 4 of molecular hydrogen.

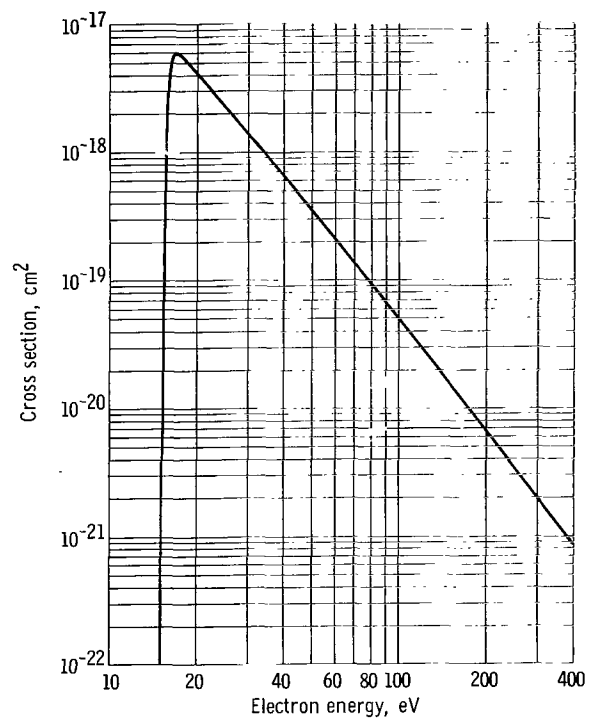


Figure 14. - Total triplet exchange cross section to levels between level 4 and ionization of molecular hydrogen. Composite exchange cross section for  $X^1\Sigma_g^+ \rightarrow (n \text{ to ionization})$ .

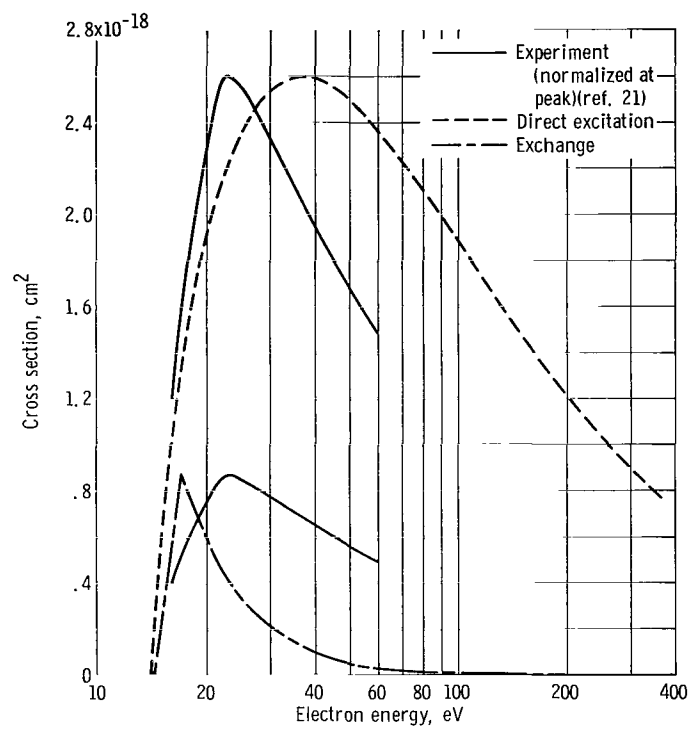


Figure 15. - Comparison of calculated singlet curve shape with experiment for molecular hydrogen. Cross section for  $X^1\Sigma_g^+ \rightarrow G^1\Sigma_g^+$ .

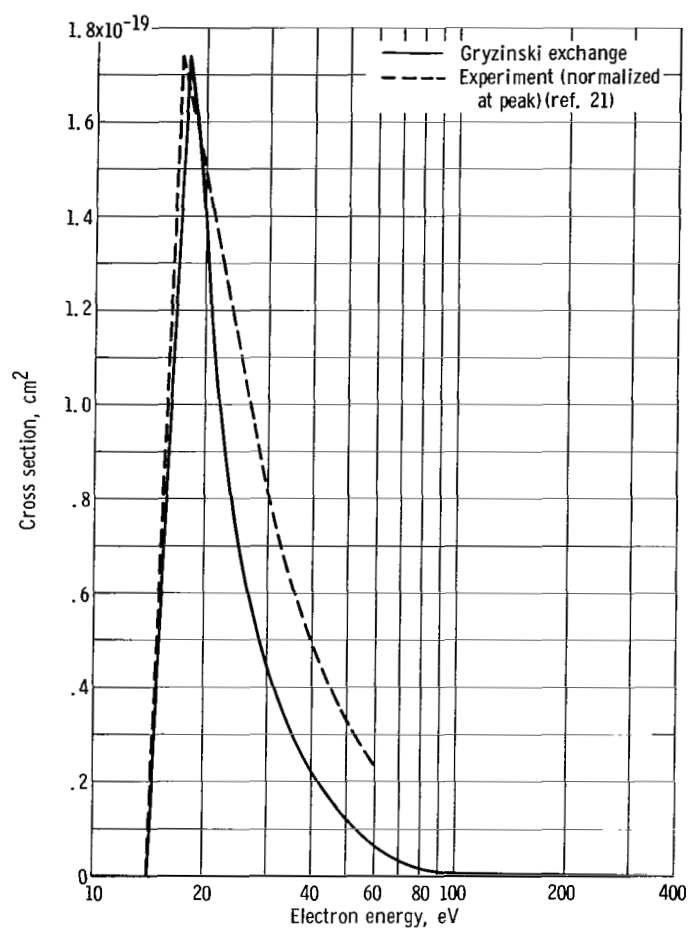


Figure 16. - Comparison of calculated triplet exchange curve with experiment of molecular hydrogen. Cross section for  $X^1\Sigma_g^+ \rightarrow k^3\Pi_u$ .

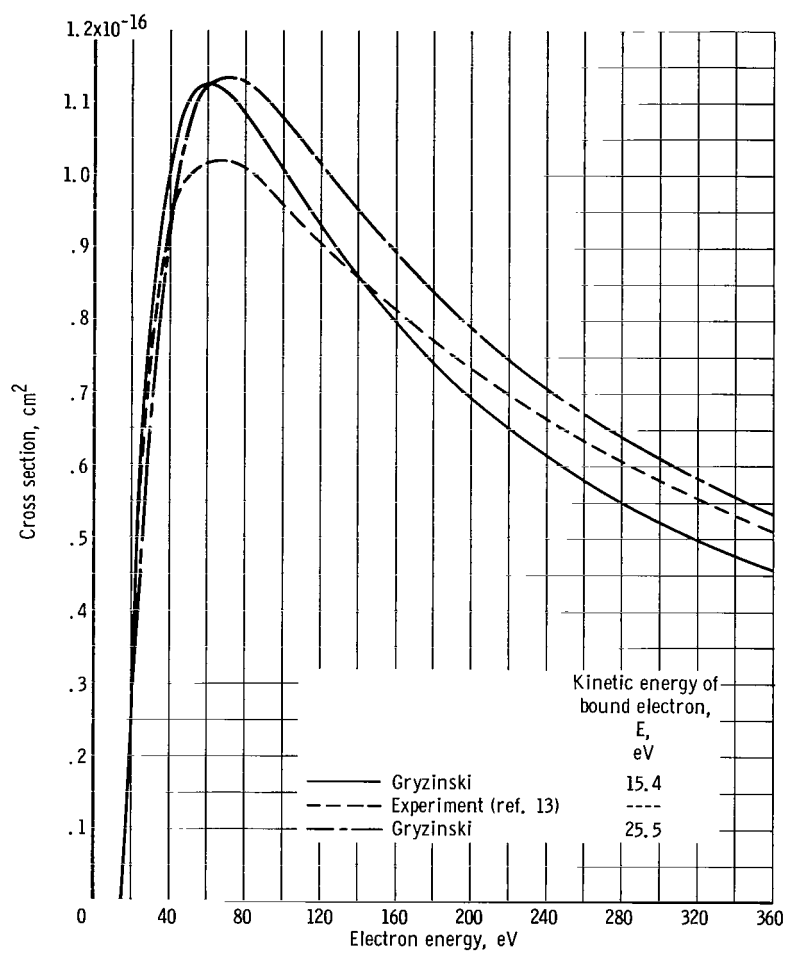


Figure 17. - Ionization cross section of molecular hydrogen. Cross section for  $X^1\Sigma_g^+ \rightarrow$  ionization.

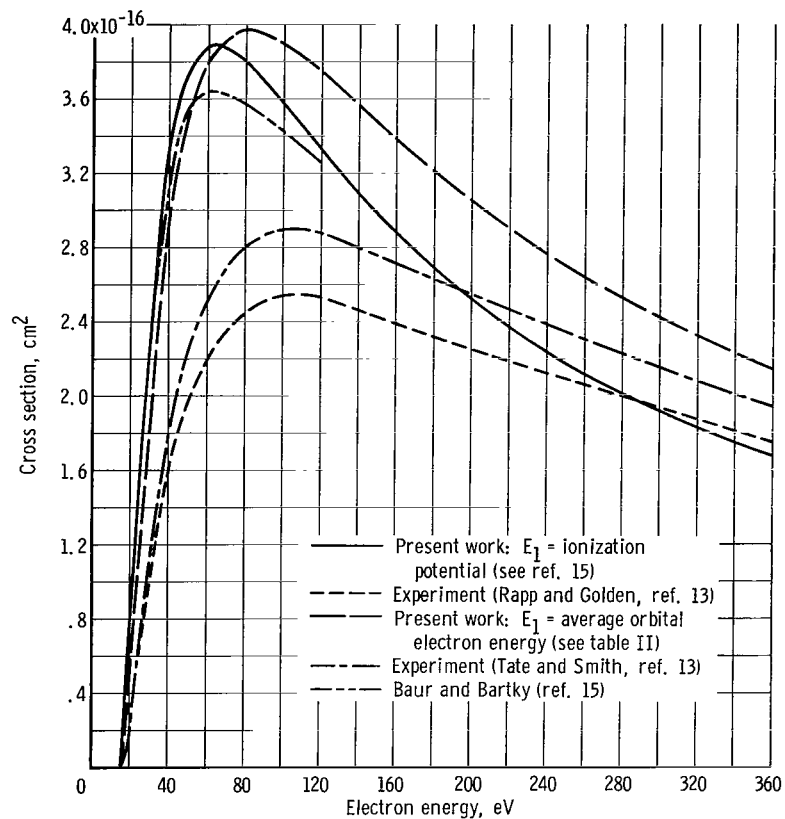


Figure 18. - Ionization cross section for molecular nitrogen.



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